

Zero preferential adsorption with carbon comes at a concentration of approximately 0.2 mole fraction of alcohol, and with silica at a concentration of approximately 0.82 mole fraction of alcohol. At zero preferential adsorption both components are adsorbed, but they are adsorbed in the same proportions as represented by the concentration of the bulk of the solution.

Summary

1. In a study of the adsorption by silica from non-aqueous binary systems over the entire concentration range the interferometric method was used to measure changes in concentration of solutions.

2. In each system investigated an S-shaped adsorption curve was obtained. Over some portion of the concentration range each of the components was preferentially adsorbed.

3. The adsorption curve obtained with silica as adsorbent is very nearly the inverted and reverse form of that obtained with carbon for the same binary liquid system.

4. That component having the higher adhesion tension against the solid is preferentially adsorbed over the greater portion of the concentration range.

5. The Freundlich equation when so modified as to express the measure of adsorption in terms of change in concentration, as

$$H\Delta x/m = ax^b(1-x) - b(1-x)^2x$$

was found to express the adsorption as determined over the entire range of concentration.

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ADSORPTION BY SILICA AND CARBON FROM BINARY ORGANIC LIQUID MIXTURES OVER THE ENTIRE CONCENTRATION RANGE

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Several different investigators have used different adsorbates, constituting an homologous series, in their studies of adsorption with silica.² A variety of solvents have been used in such work, but measurements

¹ The material presented in this paper is from a dissertation submitted by George H. Scheffler to the Graduate School of the University of Michigan, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1930. This paper was presented at a meeting of the Colloid Division of the American Chemical Society at Cincinnati, September, 1930.

² Bartell and Fu, *J. Phys. Chem.*, **33**, 680 (1929); Holmes and McKelvey, *ibid.*, **32**, 1522 (1928); Th. Sabolitschka, *Pharm. Z.*, **74**, 382 (1929).

have been carried out only over a limited range of concentration. The adsorbate components have usually been the fatty acids, since for these the change in concentration due to adsorption can be determined by ordinary analytical methods.

In general the results have shown that, in the different homologous series studied, adsorption from an organic solvent is positive. This is to be expected as it is known that, other factors being equal, the greater adsorption is obtained of that component which has the higher adhesion tension against the adsorbent. The adhesion tension values of the fatty acids against silica are greater than are those of the solvents used. The fatty acids, accordingly, should be preferentially adsorbed. It has been found that for the fatty acid series the adsorption is decreased as the molecular weight of the fatty acid adsorbate is increased. Since the adhesion tension values of the different fatty acids against silica are similar, the difference in degrees of adsorption is probably due to the increasing solubility tendency of the adsorbate as its hydrocarbon chain is increased.

Because of the similarity in chemical constitution of the saturated monobasic alcohols and the fatty acids it seems reasonable to expect that the order of adsorption of an homologous series of the saturated monobasic alcohols by silica from benzene should be similar to that obtained for the fatty acids from benzene. The solubility tendencies of the alcohols in benzene should increase as their molecular weights increase. This tendency then should result in a lower adsorption of the higher alcohols from benzene.

If carbon be employed as the adsorbent for the alcohol systems instead of silica, the amount of adsorption of the alcohols should be much less, for the adhesion tension values of the alcohols against carbon are lower than the adhesion tension values against silica and, also, the adhesion tension values of the alcohols against carbon are lower than the adhesion tension of benzene against carbon. In fact, it should be expected that the preferential adsorption tendency with carbon, when considered for different concentrations extending over the entire concentration range, would be just about opposite to that with silica.

Neither volumetric nor gravimetric methods are suitable for measuring the changes in concentration of alcohols due to adsorption. Such changes were therefore measured by interferometric analysis. This method was found to be satisfactory for the determination of the slight concentration changes involved in the adsorption from the systems studied.³ The accuracy of the method is high for the entire range of concentration.

Preparation of Materials.—The silica was prepared as described in a previous paper.⁴ A large quantity was prepared in order that all the samples used should have identical properties.

³ Bartell and Sloan, *THIS JOURNAL*, 51, 1637 (1929).

⁴ Bartell, Scheffler and Sloan, *ibid.*, 53, 2501 (1931).

The carbon was a purified ash-free blood charcoal.⁵ It was activated by heating for twenty minutes in a muffle furnace at a temperature of 1000°. It was cooled in dry air and was transferred directly to the adsorption flasks.

Standard methods were employed in the purification of the liquids. The middle fractions only were used in this work.

Results

The results obtained are indicated in the curves presented herewith. In order to conserve space, tables of data are not given. In Fig. 1 are

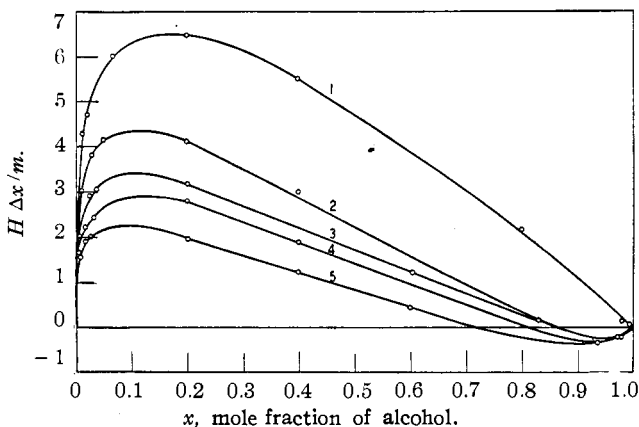


Fig. 1.—Adsorption by silica, alcohols from benzene: 1, methyl alcohol; 2, ethyl alcohol; 3, *n*-propyl alcohol; 4, *n*-butyl alcohol; 5, isoamyl alcohol.

given curves for the different alcohol-benzene systems with silica. In Fig. 2 are given the curves for the different alcohol-benzene systems with carbon. The modified Freundlich equation $H \Delta x/m = ax^n(1-x) - b(1-x)^d x$ was found to apply to all of these systems. The equations applicable to each system are:

Methyl alcohol-benzene-silica

$$H \Delta x/m = 11.429 (x)^{0.215} (1-x)$$

Ethyl alcohol-benzene-silica

$$H \Delta x/m = 8.840 (x)^{0.227} (1-x) - 4.664 (1-x)^{0.615} (x)$$

n-Propyl alcohol-benzene-silica

$$H \Delta x/m = 6.807 (x)^{0.222} (1-x) - 3.733 (1-x)^{0.684} (x)$$

n-Butyl alcohol-benzene-silica

$$H \Delta x/m = 7.261 (x)^{0.222} (1-x) - 4.808 (1-x)^{0.643} (x)$$

Isoamyl alcohol-benzene-silica

$$H \Delta x/m = 4.529 (x)^{0.216} (1-x) - 3.491 (1-x)^{0.600} (x)$$

⁵ This charcoal was furnished by E. J. Miller of the Michigan Agricultural Experiment Station.

Methyl alcohol-benzene-carbon

$$H \Delta x/m = 5.327 (x)^{0.222} (1 - x) - 12.218 (1 - x)^{0.465} (x)$$

n-Propyl alcohol-benzene-carbon

$$H \Delta x/m = 1.496 (x)^{0.616} (1 - x) - 3.819 (1 - x)^{0.323} (x)$$

n-Butyl alcohol-benzene-carbon

$$H \Delta x/m = 1.738 (x)^{0.704} (1 - x) - 3.475 (1 - x)^{0.324} (x)$$

Isoamyl alcohol-benzene-carbon

$$H \Delta x/m = 2.716 (1 - x)^{0.270} (x)$$

As indicated in Fig. 1, the preferential adsorption of the alcohols by silica from an organic solvent (benzene) having a lower adhesion tension against silica than have the alcohols, decreases as the molecular weight of the alcohols increases. Figure 2 indicates that the preferential adsorption of the series of alcohols from the same solvent by carbon is in the

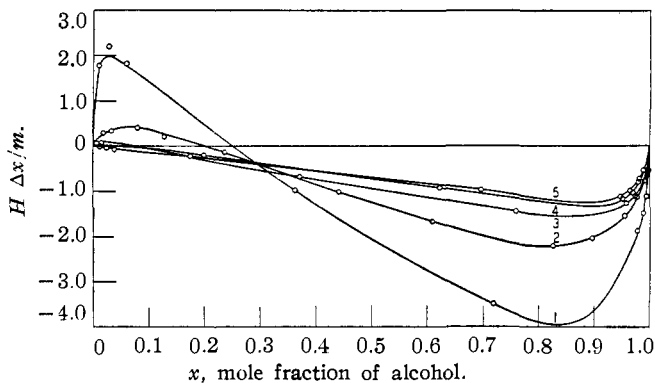


Fig. 2.—Adsorption by carbon, alcohols from benzene: 1, methyl alcohol; 2, ethyl alcohol; 3, *n*-propyl alcohol; 4, *n*-butyl alcohol; 5, isoamyl alcohol.

same order, although much less, than with silica. This is because the solvent has a higher adhesion tension against the carbon than have the alcohols. This same solvent has a relatively low adhesion tension against silica and accordingly adsorption by this adsorbent must be high.

The results obtained are consistent and are in general what were to be expected from the energy relationships of the different systems.

Two sets of results only are not as might have been predicted. The results are those obtained with the methyl alcohol-benzene system with silica and the isoamyl alcohol-benzene system with carbon. All other binary organic liquid systems which have been studied have given S-shaped adsorption curves; that is, preferential adsorption of each of the components occurred over some portion of the concentration range. With the methyl alcohol-benzene-silica system no preferential adsorption

of benzene could be detected with silica as adsorbent and with the isoamyl alcohol-benzene-carbon system no preferential adsorption of isoamyl alcohol was detected. These systems were checked repeatedly since at least a slight preferential adsorption was expected over the range indicated. Special precautions were taken to insure that perfectly dry (water-free) alcohol was used, but in no case were we able to obtain evidence of negative preferential adsorption over the range indicated.

After the completion of this work and after the paper had been written (June, 1930), a paper by Jones and Outridge⁶ appeared on "Adsorption by Silicic Acid Gel in the System *n*-Butyl Alcohol-Benzene." Adsorption of the liquid components was studied over the entire concentration range. From their results they conclude, "No region occurs, in the high equilibrium concentrations of alcohol, where there is a negative selective adsorption of the alcohol . . ." The solutions were analyzed by the "critical solution temperature" method of Jones.⁷ Their adsorption curve for the *n*-butyl alcohol-benzene system was not S-shaped. This does not agree with the results presented in this paper for this system. While we shall not at this time attempt to account for the difference in the results obtained in these two researches we have no reasons to believe that our own results covering this system are in appreciable error.

Summary

1. The monobasic alcohols of the saturated hydrocarbon series are preferentially adsorbed by silica from benzene over the greater portion of the concentration range and in an order decreasing as the molecular weight increases. The preferential adsorption by carbon from similar systems is in the same order, is of much less magnitude, and occurs over but a limited portion of the concentration range.

2. The modified Freundlich equation which has been used in other investigations recently reported from this Laboratory was found to apply to the preferential adsorption effects for both the silica and the carbon adsorbents.

3. The degree of adsorption of one component, the adsorbate, from a binary organic liquid system is dependent upon the adhesion tension of that component against the adsorbent as compared to the adhesion tension of the solvent against the adsorbent, and also upon the solubility of the adsorbate in the solvent. The effect of solubility is noted when a series of compounds of similar adhesion tensions against an adsorbent are adsorbed from a given solvent, such as benzene. The greater the solubility of the adsorbate, the less will be its tendency to be adsorbed.

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⁶ Jones and Outridge, *J. Chem. Soc.*, 1513 (1930).

⁷ Jones, *ibid.*, 123, 1392 (1923).